



Mechanical performance and microstructure array of as-cast lead–silver and lead–bismuth alloys

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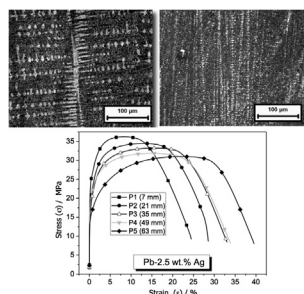
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HIGHLIGHTS

- Microstructural array affects the tensile strength of Pb–Ag and Pb–Bi alloys.
- UTS, YS (tensile strengths) and elongation were determined vs. cellular and dendritic spacings.
- Pb–Ag alloy has highest specific strength as compared with Pb–Sn and Pb–Bi alloys.
- Pb–Bi and Pb–Sn alloys examined have similar specific strengths and relative costs.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study is to establish correlations between mechanical properties of Pb–Ag and Pb–Bi alloys and parametric features of their as-cast microstructures, as well as to develop a comparative analysis with the corresponding properties of Pb–Sn alloys considering applications of these alloys in the manufacture of Pb-acid battery components. A wide range of microstructures are obtained using an upward water-cooled directional solidification system. Ultimate (UTS) and yield tensile strengths (YS) and elongation are experimentally determined as a function of cellular and dendritic spacings, and Hall-Petch type experimental equations are proposed relating UTS to these microstructure parameters. Despite the higher specific strengths of Pb–Ag alloys, as compared with those of Pb–Bi and Pb–Sn alloys, their corresponding relative costs are the highest of all Pb-based alloys examined. It is found that the Pb–Bi and Pb–Sn alloys examined have similar specific strengths and relative costs.

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1. Introduction

It is known that Pb-based alloys are widely used in the manufacture of both valve-regulated lead-acid (VRLA) and SLI battery

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components [1,2], pipes in chemical industry and water distribution system, electrical power and communication cables [3,4], electric safety fuses [5], construction of X-ray and electron radiotherapy shielding blocks [5] bearing and anodes in the electro-winning and plating [3]. Pb–Ag and Pb–Bi alloys are strong candidates among the Pb-based alloys alternatives for battery grids, since their properties can be controlled as a function of the resulting microstructure array. Investigations correlating the tensile properties of these Pb alloys with microstructure features are quite scarce in the literature. Dilute Pb–Ag alloys (i.e. between 0.7

up to 1 wt.% Ag) can be used as anode material in electrolytic zinc plants and hydrometallurgical processes [6]. Considering the Pb–Bi alloys, it was shown that grains are affected by additions of bismuth and an inverse relationship between grain size and corrosion rate was reported [7,8].

Dilute Pb-based alloys have their mechanical behavior significantly affected by solute alloying and decrease in grain size. It was also reported the considerable strengthening effect of rare earth additions to Pb-based alloys, e.g. when 2% of Pr is added to Pb, the ultimate tensile strength is 78.5% higher than that of pure Pb (20 MPa) [4]. A number of investigations [9–12] have also reported that bismuth addition (e.g. between 0.006 wt.% up to 2 wt.%) favors the corrosion resistance of Pb-based alloys.

Generally both metallurgical and solidification parameters are associated with mechanical strength and ductility since they affect the resulting as-cast microstructural morphology. A recent investigation [13,14] on dilute Pb–Sn alloys (1 and 2.5% Sn) reported that the mechanical strength was shown to be intimately associated with the resulting scale of the cellular microstructure. The ultimate tensile strength (UTS) increased with decreasing cellular spacings. This microstructural array constitutes an effective barrier to slip improving the mechanical behavior. It was also reported that the eutectic fraction (located in the intercellular regions) and solute alloying have a cooperative role in the improvement of properties of these Pb–Sn alloys [13,14]. Although silver and bismuth alloying can lead to a relative cost that is higher than those of the commonly used Pb-based alloys, their mechanical properties can be an interesting attractive depending on the final industrial application. Additionally, the relative weight can also be an industrial appealing to be considered.

In the manufacturing process of the aforementioned Pb-based alloys, a diversity of microstructural arrays can be formed. These are intimately associated with the alloy composition and the operating parameters intrinsically applied to the manufacturing process, which have important role in the control of microstructure, unsoundness, and strength [13–15]. However, studies on correlations of cooling conditions during casting, microstructural arrangement and mechanical behavior of Pb-based alloys are quite scarcely reported. The aim of this paper is to develop a comparative analysis of the mechanical performance of Pb–Ag and Pb–Bi alloys (1 and 2.5 wt.%) associated with a wide range of microstructures obtained by a directional solidification technique. Additionally, experimental correlations between the length scale of these alloys microstructure and UTS, YS and elongation are also aimed.

2. Experimental procedure

Pb–Ag and Pb–Bi alloys samples were obtained using commercially pure lead (Pb), silver (Ag) and bismuth (Bi). Table 1 shows the impurities detected by an X-ray fluorescence technique (Rigaku® Rix 3100). An upward directional solidification system was used to obtain the directionally solidified castings of Pb–Ag and Pb–Bi alloys (1 and 2.5 wt.% alloys of each system). Heat is extracted through a water-cooled bottom made of stainless steel, which promotes the upward solidification, as shown in a previous

investigation [13]. An etchant constituted by glacial acetic acid (37.5 cm³) with H₂O₂ (15 cm³) was applied to reveal the microstructures. An image processing system (Neophot 32, Carl Zeiss® linked to Leica®, Quantimet 500 MC) was used to measure the cellular (λ_c) and secondary dendritic spacings (λ_2), with average values of both λ_c and λ_2 being based on about 20 individual measurements. The tensile tests were carried out in a Test Star II® machine under a strain rate of $1.6 \times 10^{-4} \text{ s}^{-1}$ according to the ASTM standard E 8M/04. Triplicate experiments were made in order to ensure reproducibility. Specimens for tensile testing were selected from specific distances from the cooled surface of the Pb–Ag and Pb–Bi alloys castings. A representation detailing the location from where the specimens were extracted along the castings lengths is shown in Fig. 1.

3. Results and discussion

3.1. Macrostructure, microstructure and thermal parameters

Fig. 1(a) shows the macrostructures of the upward directionally solidified Pb–Ag (Fig. 1(b) and (c)) and Pb–Bi (Fig. 1(d) and (e)) alloys castings. It can be seen that columnar grains prevail from the cooled surface of the casting along the entire casting length for both Pb–Ag and Pb–Bi alloys examined.

Longitudinal sections of the microstructures of both the Pb–Ag and Pb–Bi alloys along the casting length are shown in Fig. 2. Fig. 2(a) and (b) shows the resulting microstructures of the Pb–1 wt.% Ag alloy at positions 10 and 60 mm from the cooled surface, respectively. It is important to remark that these microstructures were analyzed from samples extracted from the casting at 7 mm–10 mm from the cooled surface (named position P1). Similarly, samples from positions at 60 mm–63 mm from the casting bottom (named position P5) had their microstructures analyzed. From these microstructures, average values of both dendritic and cellular spacings were determined.

Fig. 2 (c) and (d) corresponds to samples of the Pb–2.5 wt.% Ag alloy at the same positions. Fig. 2(e) and (f) shows the microstructures of the Pb–1 wt.% Bi alloy, and (g) and (h) of the Pb–2.5 wt.% Bi alloy, respectively. A dendritic morphology characterizes the Pb–Ag alloys, while cellular arrays constitute the resulting microstructures of the Pb–Bi alloys castings.

For the Pb–Ag alloys, the Pb-rich matrix has a dendritic morphology (characterized mainly by primary and secondary arms) formed by a solid solution of Ag in Pb (light regions) with a eutectic mixture (about 2.5 wt.% Ag) in the interdendritic regions (dark regions). Tertiary dendrite arm spacings (λ_3) can also be found at positions closer to the top of the casting, as can be seen in Fig. 2(d) for the Pb–2.5 wt.% Ag alloy. This is intimately associated with the Ag content and the eutectic fraction, as previously reported [13]. The presence of tertiary arms makes the interdendritic product to be finely and homogeneously distributed throughout the microstructure. On the other hand, the Pb–Bi alloys have microstructures constituted by a cellular–matrix (Pb matrix) and an intercellular region with a Bi-rich phase, independently of the bismuth content of each Pb–Bi alloy examined. Under equilibrium cooling a solid solution of Bi in Pb should be formed, however, the water-cooled solidification system used in this investigation promoted non-equilibrium growth. This has induced a microstructure formed by a Pb-rich cellular matrix with peritectic ϵ -phase (in a tiny amount) and eutectic (ϵ + bismuth-rich phase) allocated into the intercellular regions.

The experimental variation of secondary dendritic arm spacing (λ_2) for Pb–Ag alloys and cellular spacing (λ_c) for Pb–Bi alloys as a function of: distance (D) from the cooled surface (bottom of the casting), growth rate (V_L) and cooling rate (dT/dt),

Table 1
Chemical compositions of the Pb–Ag and Pb–Bi alloys samples.

	Chemical composition (wt. %)						
	Pb	Ag	Bi	Si	Sn	Zn	Fe
Lead	balance	<0.001	N/A	<0.001	0.012	<0.001	0.08
Silver	0.0027	balance	N/A	<0.001	<0.001	N/A	N/A
Bismuth	N/A	N/A	balance	N/A	<0.001	0.01	N/A

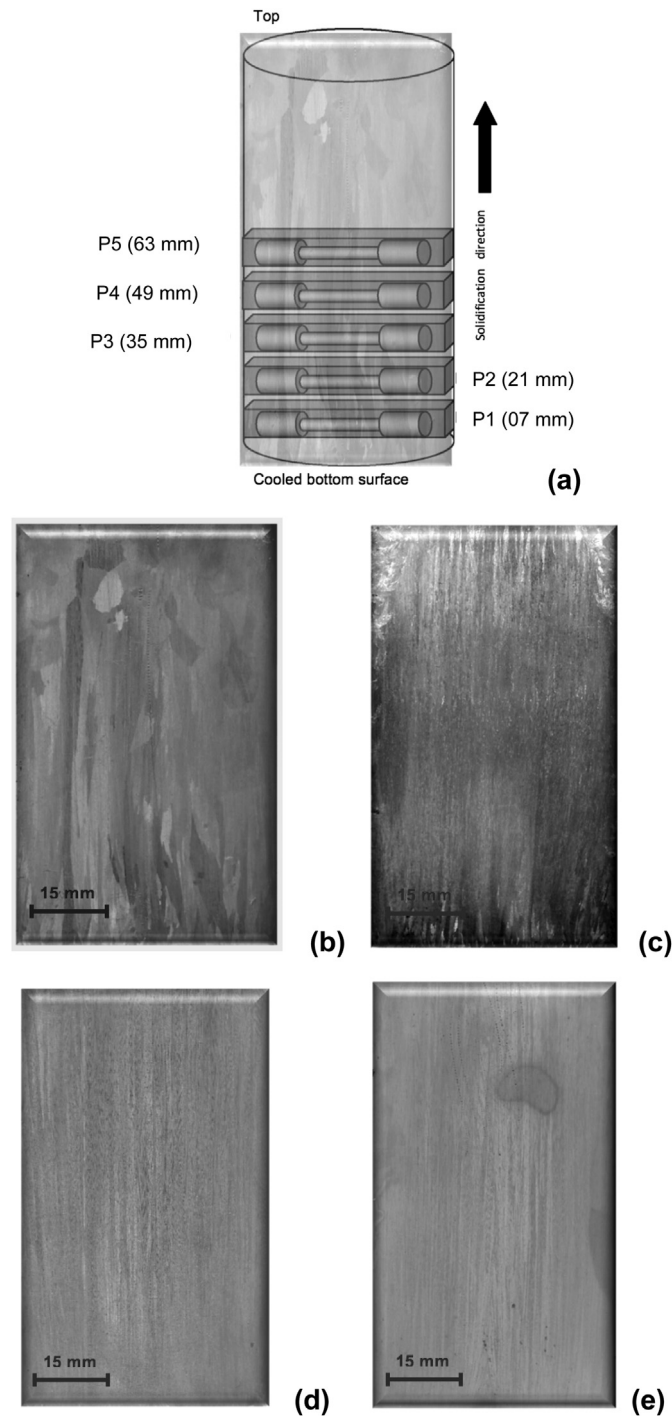


Fig. 1. (a) Representation of locations from where the specimens were extracted from the casting and typical macrostructures of upward directionally solidified castings: (b) Pb–1 wt.% Ag, (c) Pb–2.5 wt.% Ag alloys, and (d) Pb–1 wt.% Bi, (e) Pb–2.5 wt.% Bi alloys.

are shown in Fig. 3(a), (b) and (c), respectively. Finer microstructure arrays are observed near the bottom of the castings and coarser ones close to the top, which is intimately associated with the thermal solidification parameters (i.e. growth and cooling rate profiles). These parameters have high values close to the cooled surface, which decrease toward the top. Differently of the Pb–Ag alloys, which have their compositions along the castings length close to the nominal compositions, the Pb–Bi alloys

evidenced the bismuth slightly segregated at top of the casting (i.e. positions between 80 mm and 100 mm), as shown in Fig. 4. Since bismuth (9.8 g cm^{-3}) and lead (11.3 g cm^{-3}) have distinctive densities, gravity driven segregation (normal macro-segregation) could be expected. These experimental results of chemical concentration along the casting length are shown in Fig. 4, which were obtained using an X-ray fluorescence technique.

The thermocouples (Type J) positioned in specific distances from the cooled surface along the casting length, furnished thermal data from which the liquidus isotherm front passing by each specific thermocouple was measured. Lines and curves represent the empirical fit on the experimental λ_2 and λ_c points, which are expressed as a power function of D , dT/dt and V_L . It can be seen that both λ_2 for Pb–Ag alloys and λ_c for Pb–Bi alloys decrease with the increase in V_L and dT/dt , which have higher values closer to the bottom of the casting. The increase in the thermal resistance of the solidified shell with distance from the bottom of the casting causes such variation in both dT/dt and V_L with the distance.

Considering the evolution of the length scale (λ_2 and λ_c) as a function of the cooling rate (dT/dt), a -0.55 power law is derived from the experimental scatters of both Pb–Ag and Pb–Bi alloys castings. Bouchard-Kirkaldy [16] model prescribes a theoretical dendritic growth law for λ_2 vs. V_L by a $-2/3$ power law. The results of both Pb–Ag and Pb–Bi alloys can be fitted by a $-2/3$ power law. It is important to remark that slight deviations from the theoretical slope can eventually be attributed to the different metallic systems and experimental growth conditions.

3.2. Tensile tests results and examined alloys

3.2.1. Pb–Ag alloys

Fig. 5 depicts typical stress vs. strain curves of Pb–Ag and Pb–Bi alloys. Fig. 5(a) evidences stress vs. strain curves of the Pb–1 wt.% Ag alloy casting corresponding to five distinct positions from the cooled surface of the casting from where the tensile specimens were extracted, as shown in Fig. 1. Each specimen is characterized by dendritic or cellular (Pb–Bi alloys) arrays (Fig. 2) associated with cooling and growth rates (Fig. 3) that decrease from the cooled surface. In a general way, it can be said that the highest tensile strength is obtained close to the bottom of the casting, i.e. for the finest microstructural spacings, which are associated with the highest cooling and growth rates during solidification. A similar behavior can be seen with the results of the Pb–2.5 wt.% Ag alloy casting, as shown in Fig. 5(b). Comparing the tensile behavior of these two Pb–Ag alloys, it is possible to remark a common trend; an initial elastic stage followed by a small viscoplastic plateau.

For the Pb–1 wt.% Ag alloy, these plateaus are slightly characterized between $\varepsilon = 5\% (\pm 1.5)$ to $30\% (\pm 5)$. For the Pb–2.5 wt.% Ag alloy, these are clearly defined in a decreasing sequence from the position P1 to P5, i.e. in a range of strains initiating from 5% to 10% for P1, between 7% and 20% for P2, from 10% to 22% for P3, 12%–25% and 15%–30% for P4 and P5, respectively. It has been reported that these plateaus are intimately associated with a balance between work-hardening and dislocation unpinning mechanisms [13]. It is noticeable that these plateaus are displaced toward higher strain ranges with the increase in distance from the cooled surface, which is noticeable for the Pb–2.5 wt.% Ag alloy.

Another interesting observation is that silver content has induced a strengthening mechanism increasing UTS up to 50% as compared with that of the more dilute alloy. In this sense, the Pb–1 wt.% Ag alloy has ultimate tensile strengths (UTS) between 20 and

28 MPa, while for the Pb-2.5 wt.% Ag alloy UTS is in the range 30–35 MPa. The silver content has also affected the elongation (δ), with Pb-1 wt.% Ag alloy exhibiting δ between 30% and 40%, while the Pb-2.5 wt.% Ag between 20% and 30% except for position P5. It is

important to remark that the Pb-2.5 wt.% Ag alloy depicts an inverse trend for the elongation at fracture as compared with that of the Pb-1 wt.% Ag alloy. From P1 to P5, the average δ values for the Pb-1 wt.% Ag alloy were 40%, 35%, 33%, 32% and 30%, respectively.

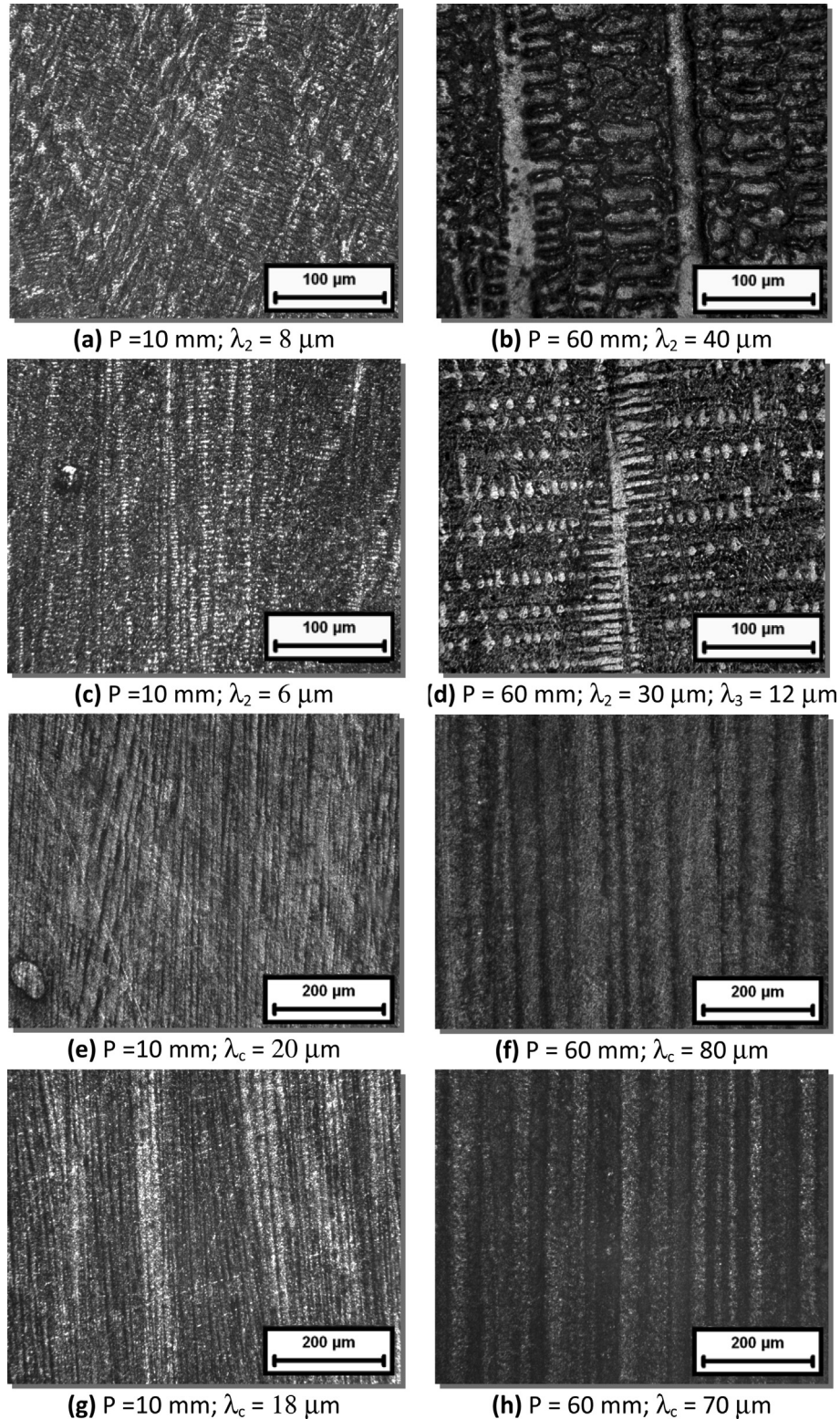


Fig. 2. Resulting microstructures of the Pb-1 wt.% and 2.5 wt.% Ag and Pb-1 wt.% and 2.5 wt.% Bi alloys, respectively at: (a) 10 mm and (b) 60 mm; (c) 10 mm and (d) 60 mm; (e) 10 mm and (f) 60 mm; and (g) 10 mm and (h) 60 mm from the cooled bottom of the casting.

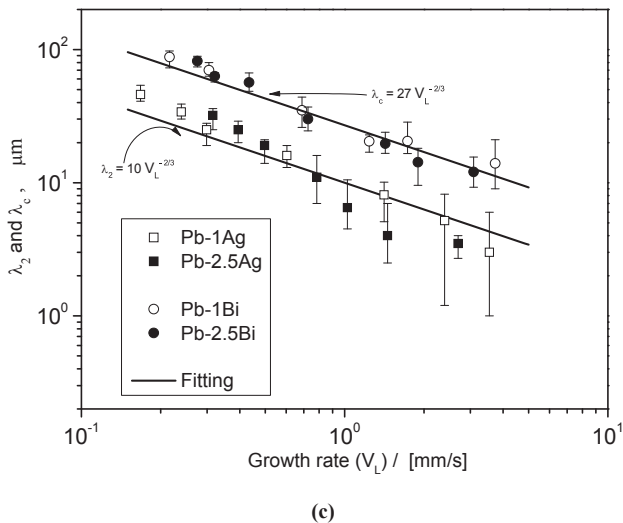
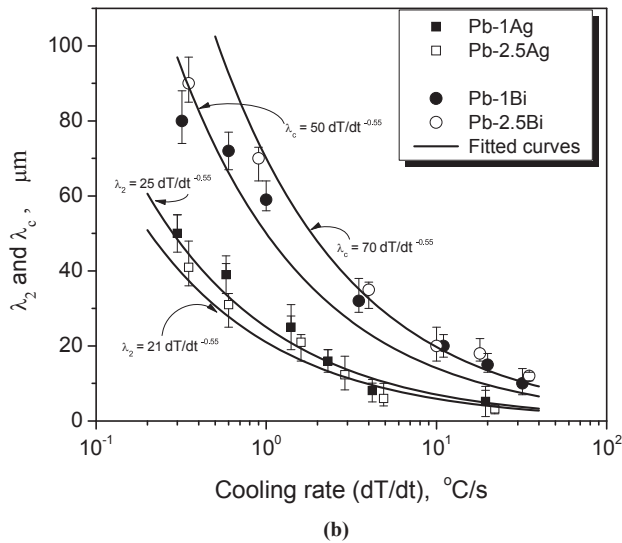
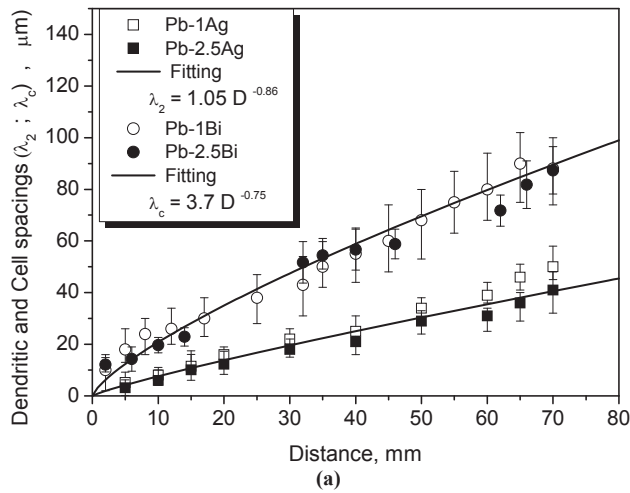


Fig. 3. Dendrite arm (λ_2) and cellular (λ_c) spacings as a function of: (a) distance from the cooled surface, (b) cooling rate and (c) growth rate for the Pb–Ag and Pb–Bi alloys castings.

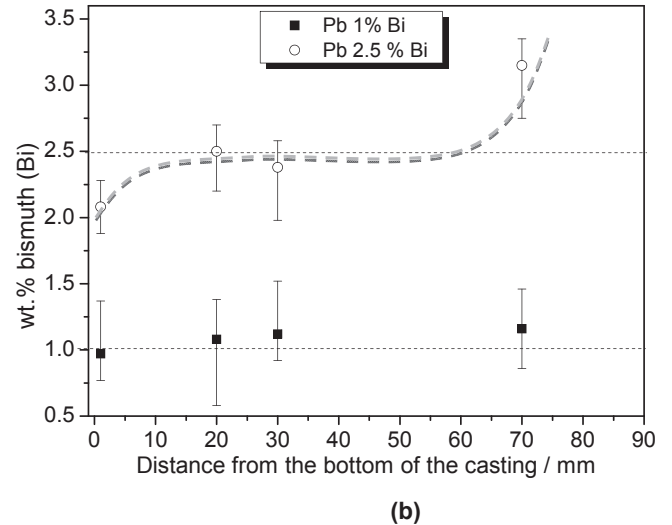
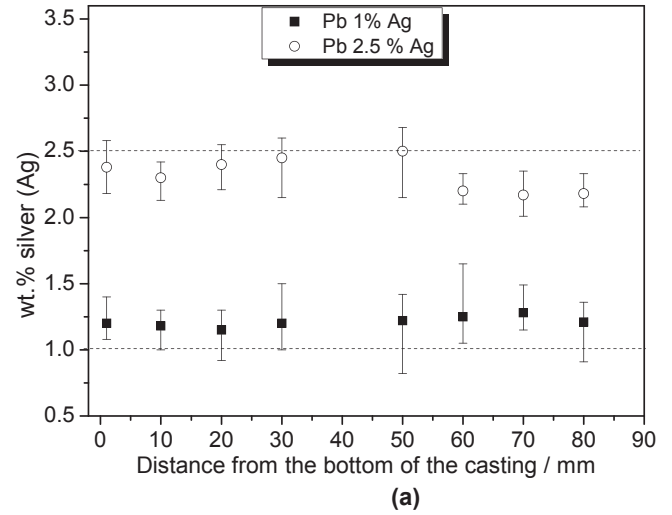
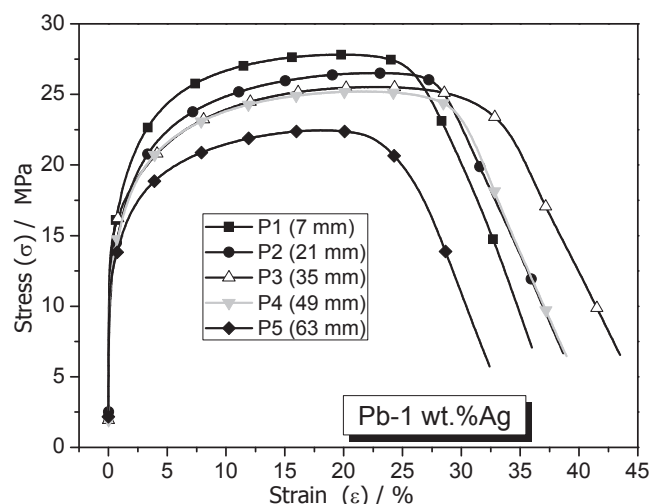


Fig. 4. Average macrosegregation of bismuth (wt.%) along longitudinal sections of the unidirectionally solidified casting for: (a) Pb–Ag and (b) Pb–Bi alloys.

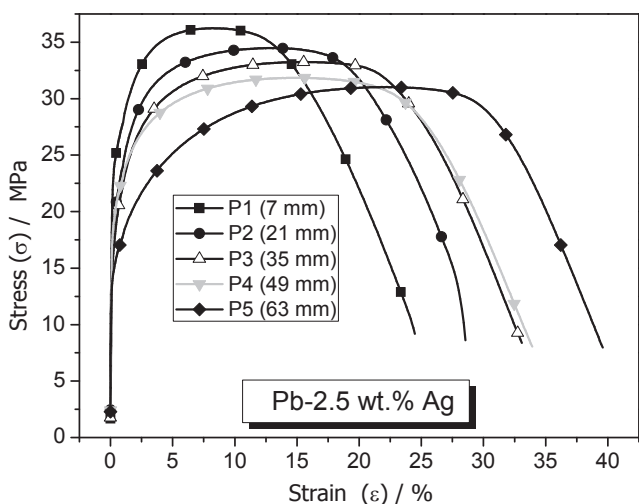
On the other hand, for the Pb-2.5 wt.% Ag alloy δ increased of about 60% from position P1 to P5. This seems to be strongly associated with the resulting microstructure array, i.e. the increase in the alloy silver content, induced the onset of tertiary dendrite arms before the position P3 (35 mm from the cooled surface). The corresponding tertiary dendritic arms (λ_3) have contributed to a more homogeneous distribution of the interdendritic phases throughout the microstructure. Higher silver content induces a higher eutectic fraction (96%), which associated with a high cooling rate during casting, determines a more homogeneous distribution of the eutectic mixture [17].

3.2.2. Pb–Bi alloys

Fig. 6 (a) and (b) shows the experimental results of the stress vs. strain curves for the Pb-1 wt.% Bi and Pb-2.5 wt.% Bi alloys castings, whose specimens were also withdrawn from the selected positions from the cooled surface bottom, as shown in Fig. 1(a). In a first observation of Figs. 5 and 6, it can clearly be seen that the Pb–Bi alloys have a UTS range of about 2 times lower (between 12 and 18 MPa) than those exhibited for the Pb–Ag alloys with similar solute content (22–38 MPa). Differently from the previously



(a)



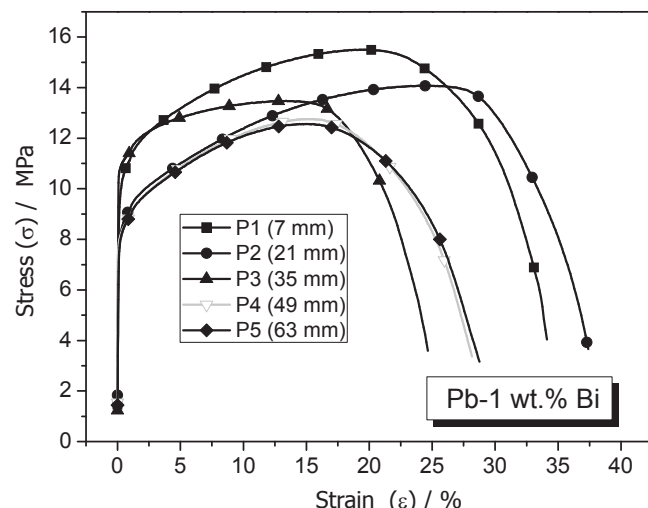
(b)

Fig. 5. Experimental stress vs. strain curves for specimens extracted at different positions from the casting cooled bottom for the: (a) Pb–1 wt.% Ag, (b) Pb–2.5 wt.% Ag alloys.

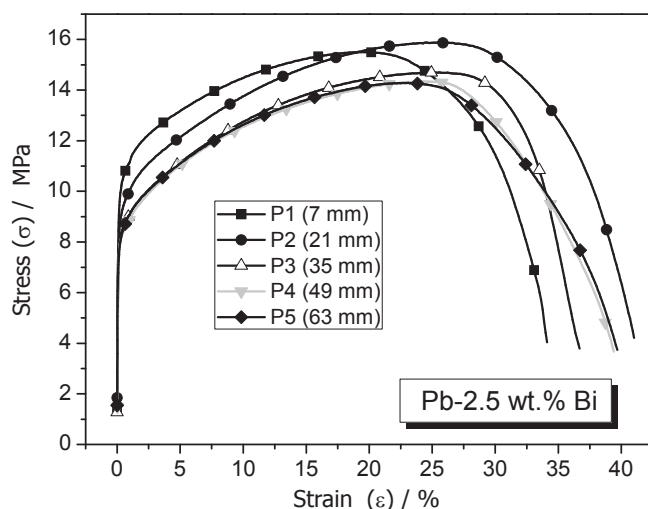
discussed results of the UTS of the Pb–Ag alloys, the Pb–Bi alloys have evidenced UTS with small discrepancies related to the solute content. However, it can also be observed a slight tendency to a decrease in UTS with the increase in distance from the cooled surface.

When analyzing positions P1 and P5 of the Pb–2.5 wt.% Bi alloy, the differences between UTS are in a range of about 50%, which is higher than those observed for the Pb–Ag alloys ($\pm 30\%$). These Pb–Bi alloys have no evidence of viscoplastic plateaus, which were clearly observed for the Pb–Ag alloys. It is important to remember that the Pb–Bi alloys have a microstructural array constituted by a cellular array, while Pb–Ag alloys has a more complex dendritic network, as previously discussed.

It seems that the Bi content has not affected the elongation. Koop et al. [7,8] reported that the Bi content affected slightly the hardness of Pb–Bi alloys. It is also interesting to observe that Pb–Bi alloys have both similar stress/strain curves and order of magnitude of UTS as compared with that of Pb–Sn alloys with similar solute contents [13,14]. The average measurements of mechanical properties (UTS, YS and elongation) of the Pb–Ag and Pb–Bi alloys



(a)



(b)

Fig. 6. Experimental stress vs. strain curves for specimens extracted at different positions from the casting cooled bottom for the: (a) Pb–1 wt.% Bi, (b) Pb–2.5 wt.% Bi alloys.

associated with distances from the cooled surface of the castings are shown in Tables 2 and 3, respectively.

3.3. Microstructure and mechanical behavior

Figs. 7 and 8 show the correlation between UTS and YS with the microstructural length scale, i.e. dendritic and cellular spacings for

Table 2

Mechanical parameters of the Pb–Ag alloys specimens examined associated with the corresponding positions in the casting.

Positions	Pb-1 wt.% Ag		Pb-2.5 wt.% Ag	
	UTS (MPa)	δ (%)	UTS (MPa)	δ (%)
P1 (7 mm)	27.8 (± 2.0)	40	36.2 (± 2.0)	23
P2 (21 mm)	26.5 (± 3.0)	34	34.5 (± 3.0)	26
P3 (35 mm)	25.5 (± 3.0)	35	33.2 (± 3.0)	30
P4 (49 mm)	25.2 (± 2.5)	32	31.8 (± 2.0)	32
P5 (63 mm)	22.5 (± 2.5)	30	31.0 (± 1.5)	37

Table 3

Mechanical parameters of the Pb–Bi alloys specimens examined associated with the corresponding position in the casting.

Positions	Pb-1 wt.% Bi		Pb-2.5 wt.% Bi	
	UTS (MPa)	δ (%)	UTS (MPa)	δ (%)
P1 (7 mm)	15.5 (± 3.0)	33	16.2 (± 1.5)	35
P2 (21 mm)	14.0 (± 2.0)	35	15.8 (± 2.0)	34
P3 (35 mm)	13.5 (± 1.0)	38	14.7 (± 2.0)	35
P4 (49 mm)	12.7 (± 2.5)	38	14.3 (± 3.0)	35
P5 (63 mm)	12.5 (± 1.5)	36	14.2 (± 2.0)	35

the Pb–Ag and Pb–Bi alloys, respectively. These values were obtained from the stress vs. strain curves shown in Figs. 5 and 6.

It is clearly observed that the Pb–Bi alloys have evidenced lower increase in UTS and YS with the microstructural spacing, as previously shown in Tables 2 and 3. However, it can also be seen that both Pb–Ag and Pb–Bi alloys have UTS increasing with the

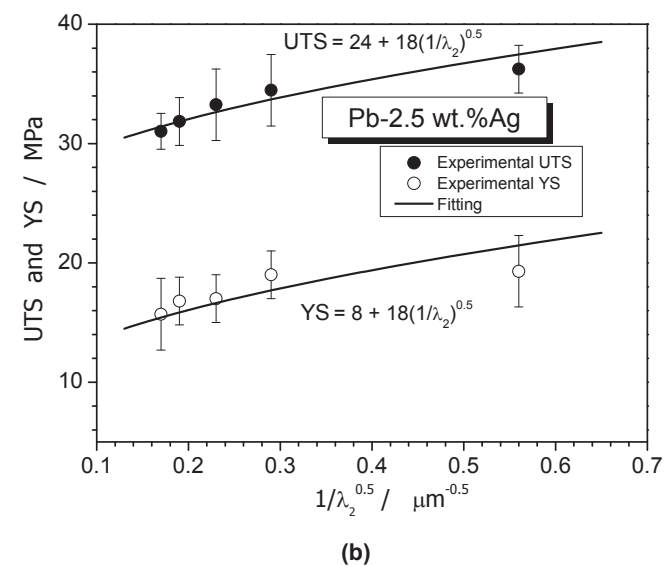
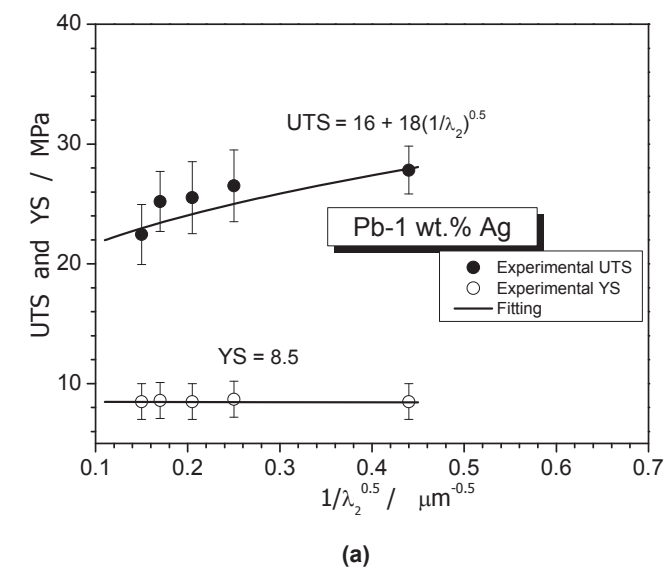


Fig. 7. Experimental results of UTS – ultimate tensile strength and YS – yield strength as a function of the secondary dendrite spacing for: (a) Pb–1 wt.% Ag alloy and (b) Pb–2.5 wt.% Ag alloys.

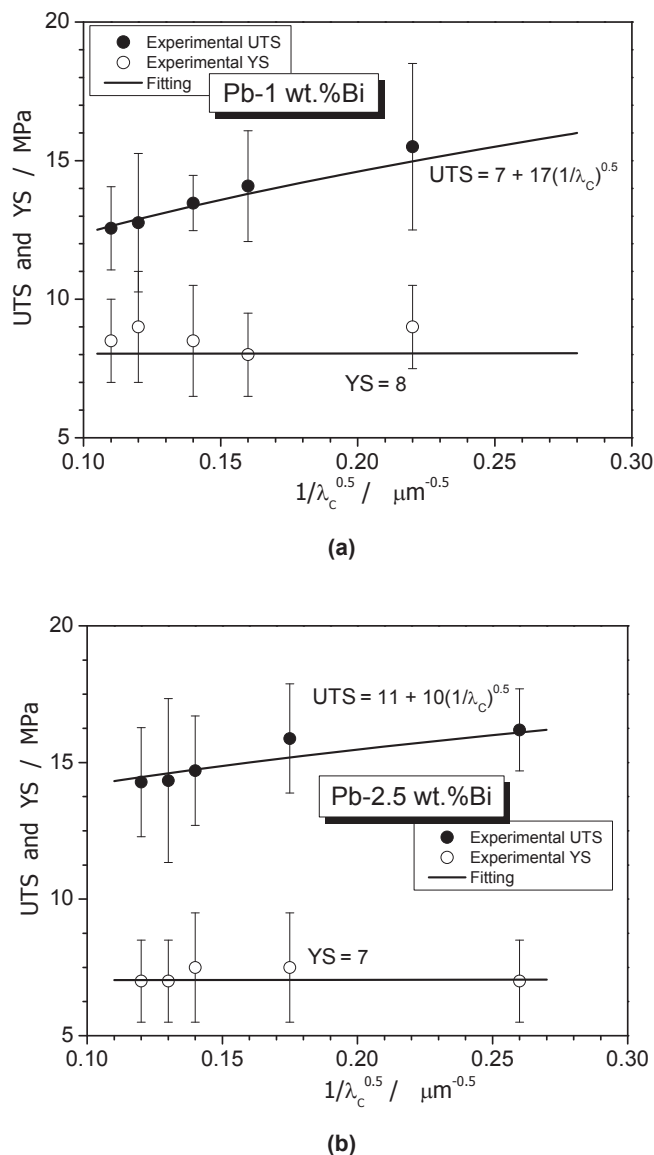


Fig. 8. Experimental results of UTS – ultimate tensile strength and YS – yield strength as a function of the cellular spacing for the: (a) Pb–1 wt.% Bi alloy and (b) Pb–2.5 wt.% Bi alloys.

decrease in the microstructure spacing, i.e. with the decrease in the dendritic and cell spacings, respectively. A finer microstructure is associated with a cleaner and sounder casting contributing for improving the resulting mechanical properties. This cannot be attributed solely to the cellular or dendritic arrangement, since the increase in cooling rate has other beneficial effects such as a decrease in gas porosity and greater solute saturation [9,18,19].

The dilute Pb-1 wt.% Ag and the two examined Pb–Bi alloys have constant YS along the castings length, i.e. the YS was not affected by the resulting microstructure. Hall–Petch type correlations have been derived by fitting the experimental scatters relating UTS and YS to both λ_2 and λ_c . It can be observed an increase in YS from 8 MPa to 17 MPa for the Pb-1 and 2.5 wt.% Ag, respectively. For the Pb–Bi alloys, the YS results have been kept at about 8 MPa. This is intimately associated with the primary interatomic forces related to bonding in the elastic range of the stress vs. strain curves. On the other hand, the permanent plastic deformation is closely related to interactions between the phases forming the

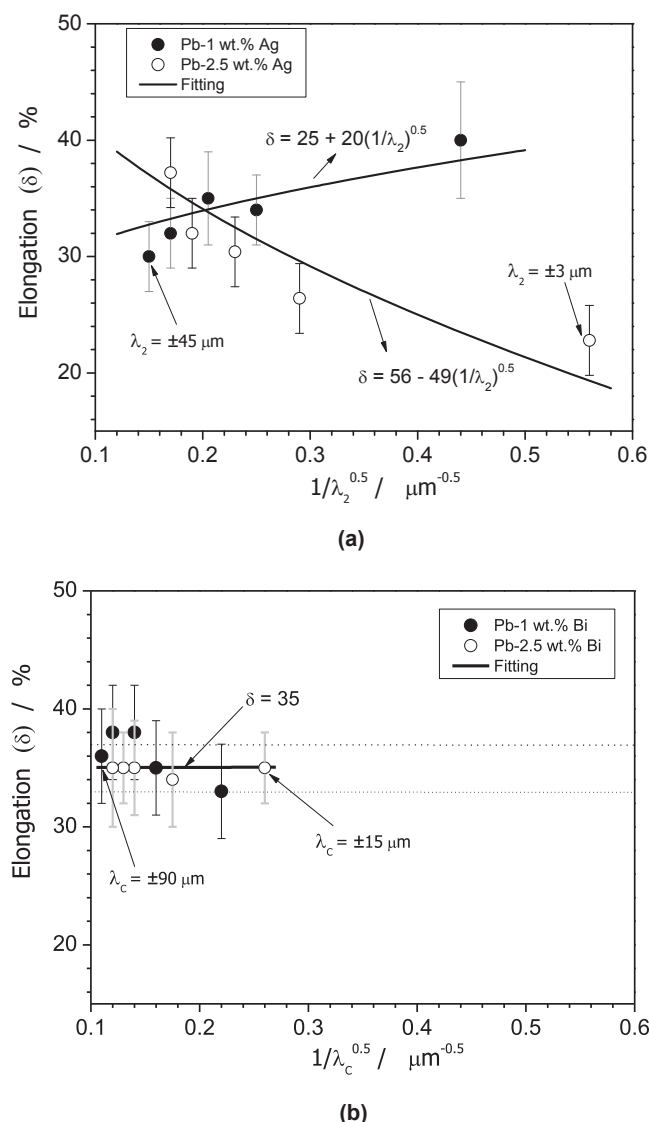


Fig. 9. Experimental results of elongation (δ) as a function of: (a) secondary dendrite spacing of Pb–Ag alloys and (b) cellular spacing of Pb–Bi alloys.

microstructure. In this sense, both cellular and dendritic spacing scales have important roles on the mechanical behavior. When YS is represented by the 0.2% proof stress, it corresponds to a stress placed already on the plastic field side of the stress vs. strain curve, so that the microstructure arrangement can have a slight role in the YS values. This can be occurred when the Pb-2.5 wt.% Ag alloy was tested, as shown in Fig. 7(b).

Considering the Hall–Petch type correlations shown in Figs. 7 and 8 and those previously obtained for the Pb–Sn alloy [13,14] with similar solute contents, some comparisons between tensile properties can be made. It can be said that from the three dilute Pb-based alloys (i.e. Pb–Sn, Pb–Ag and Pb–Bi alloys), the Pb–Bi alloy has lowest values when comparing UTS and microstructure spacings, i.e. $UTS = 7 + 17(\lambda_c)^{-0.5}$, while the Pb–Ag alloy ($UTS = 16 + 18(\lambda_2)^{-0.5}$) has a slightly advantage with respect to the Pb–Sn alloy ($UTS = 11 + 17(\lambda_c)^{-0.5}$) [13]. Analogue assertions can also be made considering the alloys with 2.5 wt.% of the solute content, i.e. the Pb–Ag alloy ($UTS = 24 + 18(\lambda_2)^{-0.5}$) has the highest correlation between UTS and microstructure spacings followed by the Pb–Sn ($UTS = 13 + 18(\lambda_c)^{-0.5}$) and Pb–Bi ($UTS = 11 + 10(\lambda_c)^{-0.5}$) alloys.

Fig. 9(a) and (b) depicts the experimental results of elongation with the microstructure spacings for both the Pb–Ag and Pb–Bi alloys, respectively. Hall–Petch type equations correlating the elongation (δ) with the dendritic spacings are also shown in Fig. 9. For the two Pb–Ag alloys examined, the Pb-2.5 wt.% Ag alloy has the elongation increased when the distance from the cooled surface of the casting is increased ($\delta = 56 - 49(\lambda_2)^{-0.5}$), i.e. with increasing dendritic spacing. This coarser microstructure array is constituted by primary, secondary and tertiary dendritic arms. This means a resulting dendritic pattern that is more complex, leading to a more homogeneous distribution of the interdendritic product throughout the microstructure. The highest elongation is associated with a position that is farther from the casting surface. On the other hand, for the Pb-1 wt.% Ag alloy the elongation to fracture decreases with the decrease in the dendritic spacing ($\delta = 25 + 20(\lambda_2)^{-0.5}$).

Considering the Pb–Bi alloys, independently of the bismuth content, it can be observed that the cellular spacing (λ_c) does not affect significantly the elongation, i.e. δ attains a order of magnitude of about 35%, as shown in Fig. 9(b). It is interesting to remark that the Pb–Ag alloys have their corresponding elongations between 20% and 40% throughout the experimental range of dendritic spacings (from $\lambda_2 = 3 \mu\text{m}$ – $45 \mu\text{m}$), while the Pb–Bi alloys have an elongation of about 35% despite the variation in the cellular spacing from about $90 \mu\text{m}$ to $15 \mu\text{m}$. Since solvent and solute have distinct densities, a typical normal macrosegregation of bismuth resulted,

Table 4

UTS, specific strength, alloy average price, relative cost of Pb–Sn, Pb–Ag and Pb–Bi alloys associated with two distinct cooling rates and the corresponding microstructural morphologies and length scales.

Alloy	Solute content	UTS MPa	Specific strength ^a $10^3 \text{ m}^2 \text{ s}^{-2}$	Average cost ^b US\$/kg	Relative cost	Cooling rate $^\circ\text{C s}^{-1}$	Microstructure
Pb–Sn	1%	12	1066	1.2–2.3	1	0.5–0.2	Cellular $\pm 95 \mu\text{m}$
	2.5%	17	1518	1.5–2.7	up to 1.25		
Pb–Ag	1%	18	1599	1.2–2.3	1	15–20	Cellular $\pm 10 \mu\text{m}$
	2.5%	20	1786	1.5–2.7	up to 1.25		
	1%	22	1949	11–22	up to 9.5	0.5–0.2	Dendrite $\pm 95 \mu\text{m}$
	2.5%	28	2482	26–52	up to 22.6		
Pb–Bi	1%	30	2657	11–22	up to 9.5	15–20	Dendrite $\pm 10 \mu\text{m}$
	2.5%	38	3369	26–52	up to 22.6		
	1%	13	1152	1.2–2.4	up to 1.04	0.5–0.2	Cellular $\pm 95 \mu\text{m}$
	2.5%	15	1332	1.7–2.9	up to 1.42		
	1%	16	1418	1.2–2.4	up to 1.04	15–20	Cellular $\pm 10 \mu\text{m}$
	2.5%	18	1599	1.7–2.9	up to 1.42		

^a Calculated based on UTS and density of each alloy.

^b Values based on LME (<https://www.lme.com/en-gb/metals>).

as shown in Fig. 4(b). It seems that the similar local composition, which is associated with the experimental macrosegregation profile of the P3, P4 and P5 specimens, is the main cause related to the similar UTS and elongation results, as shown in Table 3. The cellular spacing, λ_c , as shown in Fig. 8(b), has not a significant influence on UTS for P3, P4 and P5. As a matter of fact, as shown in Fig. 3 the spacings are not appreciably different. In contrast the influence of λ_c on UTS is significant for positions close to the cooled bottom (P1 and P2), particularly for P1 that has a local composition that is lower than the alloy nominal composition.

It is important to point out that the complexity in the microstructural pattern increases from the Pb–Bi alloys (cellular) to the Pb–1 wt.% Ag alloy (dendritic having primary and secondary arms) and increases even more for the Pb–2.5 wt.% Ag with the onset of tertiary dendritic arms. This helps also to explain the observed opposite behavior in ductility of the Pb–1 wt.% Ag and Pb–2.5 wt.% Ag alloys.

The choice between the three distinct Pb-based alloys examined in this study (i.e. Pb–Ag, Pb–Bi and Pb–Sn) associated with economical aspects and a composition combining good tensile strength as a function of the microstructural length scale, specific strength and relative cost can be made using Table 4. In order to compare the average cost of each Pb-based alloy taking into account the different solute content, the average costs were determined from the individual prices of metals constituting the examined alloys based on the metal pricing range at London metal exchange, LME (<https://www.lme.com/en-gb/metals>).

The control of thermal processing variables would control the unsoundness and strength of the Pb-based alloys castings. The average prices in US dollars per kilogram (commercially pure metals) and the relative costs with respect to the Pb–1 wt.% Sn alloy are also shown in Table 4. It can clearly be seen that the Pb–Ag alloy has the highest range of relative cost index being up to 10 times higher considering the dilute Pb–Ag alloy and of about 20 times higher than the Pb–1 wt.% Sn (taken as the reference). The intermediate values of relative costs are observed for the Pb–Sn and Pb–Bi alloys, with the dilute Pb–Bi alloy having a similar cost (1.04) as compared with that of the dilute Pb–1 wt.% Sn alloy.

The specific strengths became an important parameter to Pb-based alloys since the Pb-acid batteries manufacturers generally try to modify the grid design, processes and composition in order to decrease the battery weight without a deleterious effect on the mechanical and corrosion resistances [20,21]. The specific strengths were determined using the experimental results of UTS and the corresponding densities of each alloy considering both coarse and fine microstructures (i.e. $\pm 95 \mu\text{m}$ and $\pm 10 \mu\text{m}$, which were produced under cooling rates between 0.5 and 0.2°C s^{-1} and 15 – 20°C s^{-1} , respectively). The densities used to determine the specific strength were: 11.3 g cm^{-3} (Pb), 7.3 g cm^{-3} (Sn), 10.5 g cm^{-3} (Ag) and 9.8 g cm^{-3} (Bi). This resulted in similar densities for all Pb-based alloys examined, i.e. 11.26 and 11.2 g cm^{-3} for Pb–1 and 2.5% Sn, 11.29 and 11.28 g cm^{-3} for Pb–Ag alloys and 11.28 and 11.26 g cm^{-3} for Pb–Bi alloys.

Since the densities of all alloys examined are similar and considering similar conditions of cooling rate, it can be said that although the Pb–Ag alloys have the highest cost index (up to 20 times), their corresponding UTS (about 38 MPa) and specific strength ($3369 \text{ } 10^3 \text{ m}^2 \text{ s}^{-2}$) are higher than those of all the other alloys examined, i.e. about 2 times higher than that of the other alloys examined, as shown in Table 4. On the other hand, when the cost is taken into account, both the Pb–Bi and Pb–Sn alloys are potential candidates with a specific strength of about 12% for the Pb–Sn alloy with 2.5 wt.% of solute. Among the dilute Pb-based alloys, the Pb–Bi alloy shows compatible specific strength and interesting cost as compared with the dilute Pb–Sn alloy. Based on

these assertions, a trade-off between the specific strength and production costs (mainly induced by the solute price), should be considered for the selection of an appropriate alloy for lead-acid battery components. From the operational aspect, the manufacturers of Pb-acid batteries should consider that continuous casting produces finer microstructure, which normally increases the mechanical strength; however, the corrosion resistance can be negatively affected.

4. Conclusions

Based on the results of the present experimental study carried out with Pb–Ag and Pb–Bi alloys, compared with previous results of Pb–Sn alloys, the following main conclusions can be drawn:

- (1) It was found that finer microstructure arrays (cellular or dendritic spacings) are observed near the cooled surface of the examined castings. The fineness of these microstructures is intimately associated with higher values of growth and cooling rates.
- (2) The experimental results of UTS are intimately related to both growth and cooling rates during casting, i.e. the highest tensile strength is attained close to the bottom of the castings, associated with the finest cellular/dendritic spacings.
- (3) For the Pb–Ag alloys, it was observed that the silver content has induced a strengthening mechanism increasing UTS up to 50% and it has also affected the ductility. Another important observation was an inverse trend for the elongation at fracture of the Pb–2.5 wt.% Ag alloy as compared with that of the Pb–1.0 wt.% Ag alloy. For the former alloy the elongation increased about 60% from finer to coarser dendritic spacings. This was attributed to the onset of tertiary dendrite arms that increased the complexity of the microstructure pattern.
- (4) For the Pb–Bi alloys, UTS is shown to increase about 50%, when fine and coarse cellular spacings are compared. Besides, these Pb–Bi alloys have not evidenced viscoplastic plateaus observed for the Pb–Ag alloys examined and the bismuth content has not affected the elongation.
- (5) Since the microstructure parameters depend on the thermal solidification variables (i.e. both the growth and cooling rates) and the resulting mechanical properties are related to microstructural parameters, according to experimental relationships $\lambda_2 = f(V_L \text{ or } dT/dt)$ proposed in the present study, these can be used in the preprogramming of solidification, based on the required tensile strengths.
- (6) It was also found that Pb–Ag alloys have highest specific strength as compared with Pb–Sn and Pb–Bi alloys with similar solute content. However, their corresponding relative cost is up to 20 times higher than those of the Pb–Bi and Pb–Sn alloys. Both Pb–Bi and Pb–Sn alloys can be considered appropriate choice of Pb-based alloys for battery components when the relative cost is taken into account.

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